STXM Characterization of Crosslink Density in SAP

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INTRODUCTION

Customer demand for thinner diapers and other hygiene products has been leading manufacturers to decrease the amount of cellulose fluff and increase the proportion of superabsorbent polymer (SAP) used in their products. This increases the need for gel strength (weight bearing capacity) of the hydrated SAP so that they maintain their water absorption under load [1] In order to meet the demands for the higher liquid absorption under load while maintaining liquid capacity, Dow and most other suppliers of superabsorbent polymers are using structured particle technology to enhance the strength of their material. These so called third generation superabsorbent polymers are crosslinked in a core-shell structure to improve liquid absorbence under load. Other than macroscopic tests to measure the liquid absorption capacity of the modified SAP, until recently there has been no method to determine the structure of these materials. In an effort to provide feedback for improvements in the process chemistry, we have been developing methodology to apply conventional and scanning transmission x-ray microscopy (CTXM and STXM) to examine water swollen experimental superabsorbent polymers which had been crosslinked in different ways. Since the relationship between degree of swelling and crosslink density is well established[2], we can determine the microscopic variation in crosslink density from the polymer density in the hydrated SAP. To date no other characterization method has been able to demonstrate sensitivity to the variations in crosslink density at the spatial scale available by STXM.

In work reported previously, we demonstrated that we could visualize the variation in crosslink density in core / shell type superabsorbent polymers using STXM [3]. These results can be very useful in understanding the effect of variations in crosslink chemistry and process parameters. Experiments performed during the last year have focused on quantifying the crosslink density on the submicron scale. The microscopic variation in the polymer density can be determined from the x-ray absorption intensity in STXM with a 50 nm spatial resolution.

RESULTS

The intensity of x-rays transmitted through a sample of thickness z is given by Beer's law:

$$I = I_0 \exp\{-\mu(E)\rho z\} \qquad (1)$$

where $\mu(E)$ is the energy dependent mass absorption coefficient, ρ is the density and I_0 is the incident x-ray intensity. For multiple chemical species in the sample, the absorption by the different speces is additive so that for the system of interest with water and polymer present at the same time equation 1 becomes:

$$\ln I/I_0 = \mu_{poly}(E)\rho_{poly}z + \mu_{water}(E)\rho_{water}z \qquad (2).$$

By determining the energy dependent mass absorption coefficient and making the x-ray absorption measurements at two different energies, equation 2 can be solved to determine the polymer density. If images are recorded at two different energies, then the polymer density can be determined at every pixel of the image. Similar analytic methods have been used by Zhang et al. to map the DNA in sperm cells using STXM [4].

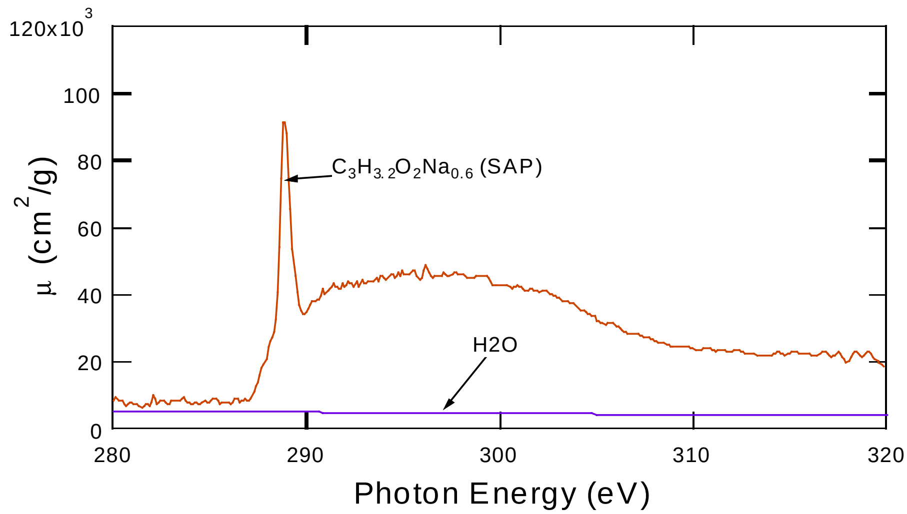

Figure 1. Mass absorption coefficient for superabsorbent polymer in the near edge spectral region (280-340 eV) compared to that for water at the same energy.

The x-ray absorption cross sections for all the elements have been tabulated as a function of energy by Henke, Gullikson and Davis, and are accurate for energies sufficiently far from an ionization threshold [5]. Near the threshold, the NEXAFS spectrum must be measured. Figure 1 is a plot of the mass absorption coefficient for water, and for superabsorbent polymer (80% neutralized sodium polyacrylic acid). The latter was determined by fitting a measured NEXAFS spectrum to the tabulated value of the mass absorption coefficient [5] below and above the near edge region (280 and 320 eV). The NEXAFS spectrum of SAP has an intense peak at 288.8 eV which is attributed to an electronic transition from a C(1s) orbital to the π*(C=O) orbital on the acrylate C atom. This is the energy which provides the best contrast between water and polymer for STXM images (factor of 16 difference in cross sections). At 280.0 eV the photoabsorption cross sections for the two materials are similar.

In the example in Figure 2, we have examined a microtomed thin section of a spherical experimental SAP bead at 280.0 eV (below the C(1s) edge and at 288.8 eV (which is the peak absorption energy for the C(1s) → π*(C=O) transition of the acrylate carbon). The sample is completely hydrated in 0.9% salt water and there is excess salt water in the cell. In the 288.8 eV image the polymer section is clearly observable and the higher crosslinked shell can be seen near the edge of the sample as an arc across the top half of the image. Measurements of the swelling of these samples prior to crosslinking the surface, determined that the core of this SAP sample absorbs 68 times its' weight in water. Though the higher crosslinked shell will absorb somewhat less water, because of the similar absorption cross sections for water and polymer, and the excess water in the cell (up to 3 μm thick), at 280.0 eV, the polymer is invisible. From the latter image, a gradient in the water layer thickness can be discerned, with decreasing thickness from top to the bottom. Utilizing the known and measured x-ray absorption cross sections for water and

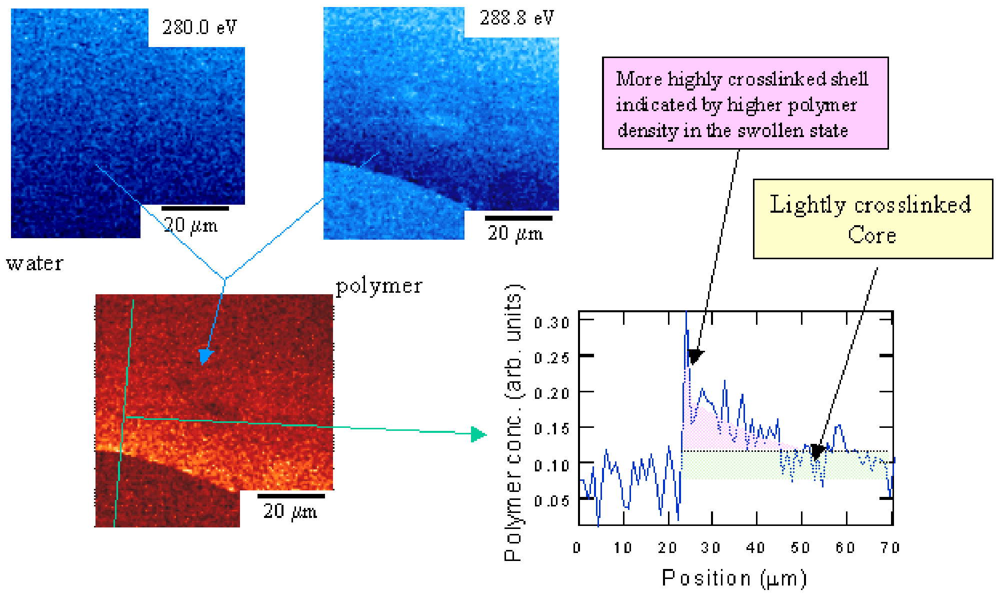

Figure 2. STXM images measured at 280.0 and 288.8 eV photon energy (top) and the polymer density calculated from these images (bottom left). At the bottom right is a plot of the polymer density extracted from the image at left along the indicated line to highlight the core / shell structure of the crosslinking in this sample of experimental SAP.

polymer and the additivity of the x-ray absorption cross sections, we can solve equation 2 to calculate (on a pixel by pixel basis) the image at the center of Figure 2 in which the intensity is in terms of polymer concentration. From this data and the Flory Rehner equation [2], the crosslink density can be also easily determined on a pixel by pixel basis.

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